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Review

Discrete metal complexes from *N*-heterocyclic ferrocenes: structural diversity by ligand design

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ABSTRACT

The aim of this review is to provide an overview of the structures of discrete metal complexes with *N*-heterocyclic ferrocenes, based on their crystal structures. These *N*-heterocyclic ferrocenes act as versatile ligands for the construction of metal complexes with unique structures, owing to the $\pi\cdots\pi$ interaction between the *N*-heterocycles and conformational flexibility of the ferrocenyl moiety. *N*-Heterocyclic ferrocenes coordinate to metal ions in monodentate, C,N-bidentate, multidentate, and bridging fashions, which results in metal complexes with various M:L stoichiometry. The ligands and their metal complexes have been recently employed for applications including chemical sensors, homogeneous catalysts, and redox-driven conformational switching.

Keywords: *N*-Heterocyclic ferrocene; Coordination mode; Crystal structure

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Contents

1. Introduction
2. Structures of metal complexes
 - 2.1. *N*-Heterocyclic ferrocenes that produce monodentate complexes
 - 2.1.1. Pyrazole and triazole derivatives (**L1–L4**)
 - 2.1.2. Pyridine, pyrimidine, and pyrazine derivatives (**L5–L9**)
 - 2.1.3. Naphthyridine derivative (**L10**)
 - 2.2. *N*-Heterocyclic ferrocenes that produce metallacycle complexes
 - 2.2.1. Imidazoline derivatives (**L11, L12**)
 - 2.2.2. Pyridine and pyrimidine derivatives (**L13–L15**)
 - 2.2.3. Bipyridine, quinoline, and phenanthroline derivatives (**L16–L19**)
 - 2.3. *N*-Heterocyclic ferrocenes that produce chelate complexes
 - 2.3.1. Pyrazole and triazole derivatives (**L20–L23**)
 - 2.3.2. Bipyridine and pyrimidine derivatives (**L16, L24**)
 - 2.3.3. Terpyridine and polypyridine derivatives (**L25, L26**)
 - 2.3.4. Hydroxyquinoline and phenanthroline derivatives (**L27, L19**)
 - 2.4. *N*-Heterocyclic ferrocenes that produce macrocyclic complexes
 - 2.4.1. Pyrazole derivative (**L1**)
 - 2.4.2. Pyridine and pyrazine derivatives (**L28–L31**)
 - 2.4.3. Quinoline and naphthyridine derivatives (**L32, L33**)
3. Summary and future outlook
- Acknowledgments
- References

Abbreviations: Ac, acetyl; acac, acetylacetonato; bpy, 2,2'-bipyridine; *t*-Bu, tertiary-butyl; cod, 1,5-cyclooctadiene; Cp, cyclopentadienyl; Cy, cyclohexyl; dcpab, 2-dicyclohexylphospanyl-2'-(*N,N*-dimethylamino)biphenyl; dppe, diphenylphosphinoethane; dppf, 1,1-diphenylphosphinoferrocene; dppp, diphenylphosphinopropane; dppz, dipyridophenazine; hfac, 1,1,1,5,5,5-hexafluoroacetylacetonate; OTf, trifluoromethanesulfonate; PEG, poly(ethylene glycol); Ph, phenyl; phen, 1,10-phenanthroline; PPN, bis(triphenylphosphine)iminium cation; *i*PrNHC, 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene; H-ptpy, 2-(4-tolylpyridine); TBAB, tetra-*normal*-butylammonium bromide; [14]aneS₄, 1,4,8,11-tetrathiacyclotetradecane.

1. Introduction

Ferrocene derivatives have been widely utilized in various fields, mainly owing to their unique structural, electronic, and magnetic properties [1–3]. In particular, synthesis and applications of ferrocene derivatives as ligands have been reported extensively [1–3]. However, *N*-heterocyclic ferrocenes, defined here as ferrocenes with *N*-heterocyclic substituents on their cyclopentadienyl rings, have received less attention as ligands. These groups are rich in synthetic chemistry and structural chemistry [4–8]; however, they have only recently been employed as ligands in coordination chemistry. There are several advantages for using *N*-heterocyclic ferrocenes as ligands. First, they show interesting coordination chemistry owing to the variety of *N*-heterocycles (Fig. 1) and the conformational flexibility of ferrocene rings and *N*-heterocycles (Fig. 2). Second, functionalized building blocks, especially metal-containing ligands (metalloligands) [9–11], have been the subject of recent attention in crystal engineering [12, 13]. In fact, the introduction of a ferrocenyl group to an *N*-heterocyclic ring is a rational approach to obtain metalloligands. Third, *N*-heterocyclic ferrocenes and their metal complexes have proven to act as chemical sensors [14–19], homogeneous catalysts, and conformationally switchable materials, taking advantage of the conformational flexibility and redox ability of the ligands. Finally, many of these systems have well-defined structures, which allows for a better understanding of their properties.

In this review, we discuss the structural variation of the discrete metal complexes with *N*-heterocyclic ferrocenes based on crystallographic data. Complexes without crystallographic data will be described only when they have remarkable aspects. Omitted from this review are ferrocenes bearing chiral *N*-heterocycles, saturated *N*-heterocycles, and mixed donor *N*-heterocycles, which have considerable use as ligands for asymmetric catalysts, because they have been reviewed in the literature [20–23]. Also omitted are coordination polymer complexes with *N*-heterocyclic ferrocenes, which are summarized in our previous review [11].

2. Structures of metal complexes

All *N*-heterocyclic ferrocenes in this review are classified according to their coordination fashion and ring size (Fig. 3). *N*-Heterocyclic ferrocenes can be prepared by general synthetic procedures, including palladium catalyzed cross-coupling [24–31], cyclodehydration [32–39], azide alkyne Huisgen cycloaddition (Click reaction) [14, 15, 40, 41], and other reactions [42–46].

2.1. *N*-Heterocyclic ferrocenes that produce monodentate complexes

Structural formulae of *N*-heterocyclic ferrocenes adopting monodentate ligation are summarized in Fig. 4. The chemical formulas of their complexes are listed in Table 1. Although the *N*-heterocyclic ferrocenes dealt with in this section are simple, their coordination structures vary, accompanying the variation of the M:L ratios. Ferrocenes with bulky *N*-heterocycles, such as indole [47], benzimidazole [37], perimidine [48], quinoline [30, 32, 39, 43], and quinoxaline [33–36, 38], also act as monodentate ligands; however, their metal complexes are fewer.

2.1.1. Pyrazole and triazole derivatives (**L1**–**L4**)

Although many ferrocenyl pyrazole derivatives have been reported, their coordination complexes are relatively few. The photochemical reaction of **L1**·H and W(CO)₆ affords a 1:1 M:L complex [W(CO)₅(**L1**·H)] (**1**, Fig. 5) [49]. The crystal structure of **1** reveals that the pyrazole of **L1**·H coordinates to the tungsten(II) center with the nitrogen atom farther away from the ferrocenyl moiety. The N–H group of **1** forms an intermolecular hydrogen bonding with a carbonyl moiety of an adjacent molecule to construct a 1D network structure.

L2·H, a regioisomer of **L1**·H, coordinates to a metal(II) ion via the 2-position nitrogen to construct 1:4 or 1:2 M:L complexes, [MX₂(**L2**·H)_n] {M = Zn, X = NO₃[−], n = 4 (**2**, Fig. 6a); M = Co, X = Cl[−], n = 4 (**3**, Fig. 6b); M = Zn, X = NCS, n = 2 (**4**, Fig. 6c)} [50]. **2** and **4** possess 1D hydrogen bonding network structures, while **3** shows a discrete structure. **2** has two polymorphs, **2a** and **2b**. Despite the difference in their packing structures and space groups (*P*-1 for **2a**, *P*2₁/*c* for **2b**), their

molecular structures and the hydrogen bonding networks are almost the same. The metal(II) ions in **2a** and **3** adopt an octahedral geometry and are occupied by four equatorial nitrogen atoms from four **L2·H** ligands and two axial heteroatoms from counter anions. In **2a**, two of the four **L2·H** ligands form intramolecular N–H···O hydrogen bonds with two NO₃[−] anions, while the others form intermolecular N–H···O hydrogen bonds with two NO₃[−] anions from two adjacent molecules, affording a 1D network structure. The zinc(II) ion in **4** shows a tetrahedral coordination geometry, surrounded by four nitrogen atoms from two **L2·H** ligands and from two NCS[−] anions. Each unit is linked by intermolecular N–H···S hydrogen bonds between two ligands and two counter anions, forming a 1D network structure.

Several ferrocenyltriazole derivatives and their coordination complexes have been prepared during the development of the Click reaction [14, 40]. By treating with PdCl₂(PhCN)₂, **L3** and **L4** afford [PdCl₂(**L**)₂] {**L** = **L3** (**5**, Fig. 7) [51] and **L4** (**6**) [52], respectively}. The palladium(II) centers in both **5** and **6** show square planar coordination geometry, in which the *N*-donor ligands occupy the *trans* positions. In both complexes, the ligands coordinate to the metal center with the nitrogen atom farthest away from the benzyl group. A trinuclear ferrocenyltriazole derivative can be also prepared using the Click reaction of the trifunctionalized benzene derivative and ethynylferrocene, and this derivative reacts with β-cyclodextrin to form an encapsulated complex (Fig. 8). The complex can stabilize and solubilize palladium nanoparticles, which catalyze both the Suzuki and Heck reactions in aqueous media [53].

2.1.2. Pyridine, pyrimidine, and pyrazine derivatives (**L5–L9**)

The most widely investigated class of *N*-heterocyclic ferrocenes has been those with six-membered rings. Many complexes with **L5** and **L6** are crystallographically characterized. Most studies on the complexes with **L6** deal with their electrochemical properties, which have revealed that there is little electronic communication between the ferrocenyl group and the metal center [54–58]. Because of the similarity of the complexes, we will limit our discussion to certain interesting 1:2 and 2:2 M:L complexes with **L5**, [MCl₂(**L5**)₂] {M = Pd (**7**, Fig. 9a) [59], Pt (**8**, Fig.

9b) [60]}, and $[\text{Au}(\text{C}_6\text{F}_5)(\mathbf{L5})]_2$ (**9**, Fig. 9c) [61]. The two **L5** ligands in **7** occupy the *trans*-positions of the palladium(II) center, while those in **8** coordinate to the *cis*-positions of the platinum(II) center. The assembled structure of **9** can be regarded as a 2:2 M:L dimer, in which the gold(I) centers adopt a slightly distorted T-shaped geometry and are bounded by a nitrogen atom from **L5**, a carbon atom from C_6F_5 , and an adjacent gold(I) ion ($\text{Au}\cdots\text{Au} = 3.301(2) \text{ \AA}$). In the dimer, the pyridyl moiety of **L5** and the adjacent C_6F_5 ring lie approximately parallel and are separated by 3.58 \AA , which is an acceptable distance for $\pi\cdots\pi$ stacking interaction [62]. The structures of $[\text{RhCl}(\text{cod})(\mathbf{L5})]$ [63], $[\text{Au}(\mathbf{L5})(\text{PPh}_3)]$ [61], $[\text{Au}(\text{C}_6\text{F}_5)_n(\mathbf{L5})_m]$ ($n = 2, m = 2$; $n = 3, m = 1$) [61], and $[\text{RuCl}(\mathbf{L6})\{[14]\text{aneS}_4\}]\text{Cl}$ [54] are similar to the above ones.

The reaction of $\text{PdCl}_2(\text{CH}_3\text{CN})_2$ and the diferrocene **L7** generates the 1:2 M:L complex $[\text{PdCl}_2(\mathbf{L7})_2]$ (**10**, Fig. 10) [64], in which the square planar palladium(II) center is coordinated by the *trans* nitrogen atoms from two **L7** ligands and two chlorine atoms. The two **L7** ligands adopt a head-to-head conformation around the palladium(II) center in which the ferrocene groups adopt the anti conformation with respect to the central pyridine ring. The angles between the pyridyl and Cp rings in the complexes with **L5–L7** vary between 3.3 and 52.3° . A similar variation is found in the complexes with **L8**.

L8 is a versatile ligand that coordinates to a variety of metal ions to generate discrete complexes or coordination polymers [11, 65, 66]. In the 2:2 M:L complex $[\text{Cu}(\text{OAc})_2(\mathbf{L8})]_2$ (**11**, Fig. 11a) [65], one of the two pyrimidine rings shows intermolecular $\pi\cdots\pi$ interactions (3.59 \AA). The 1:2 M:L complex $[\text{Zn}(\text{NCS})_2(\mathbf{L8})_2]$ (**12**, Fig. 11b) also possesses a dimer-like structure with an effectual $\pi\cdots\pi$ interaction between the Cp ring and pyrimidine ring of an adjacent molecule (3.58 \AA) [65]. The choice of solvent for the complexation of **L8** and $[\text{Ni}(\text{hfac})_2]$ is critical; the reaction in diethyl ether generates a 1:2 M:L discrete complex, $[\text{Ni}(\text{hfac})_2(\mathbf{L8})_2]$ (**13**, Fig. 11c) [67], while the reaction in pentane leads to a zigzag side chain polymer, $[\text{Ni}(\text{hfac})_2(\mathbf{L8})]_n$ [66], having an M:L ratio of 1:1, regardless of the initial M:L ratio during synthesis. Two **L8** ligands in **13** act as monodentate ligands and occupy the *cis* positions of the nickel(II) center. This contrasts with the result of $[\text{Ni}(\text{hfac})_2(\mathbf{L8})]_n$, in which **L8** behaves as a bidentate bridging ligand and occupies the *trans*

positions of the nickel(II) center. The 1:3 M:L complex $[\text{Zn}(\text{NO}_3)_2(\text{L8})_3]$ (**14**, Fig. 11d) possesses a five-coordinated distorted square pyramidal zinc(II) center [65], in which two nitrogen atoms from two **L8** ligands, two oxygen atoms from two counter anions occupy the equatorial positions, and a nitrogen atom from the remaining **L8** occupies the axial position. The 1:4 M:L pinwheel-like complex $[\text{Ni}(\text{NCS})_2(\text{L8})_4]$ (**15**, Fig. 11e) contains a nickel(II) ion with a distorted octahedral geometry in which four **L8** ligands occupy the equatorial position [67], and the two NCS^- groups are in the axial positions. The reaction of *cis*- $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$ and **L8** in the presence of AgPF_6 generates $[\text{cis-Pt}(\text{NH}_3)_2(\text{L8})_2](\text{PF}_6)_2$ (**16**), which transforms to $[\text{trans-Pt}(\text{NH}_3)_2(\text{L8})_2](\text{PF}_6)_2$ (**17**) on heating [68]. The NH_3 groups in the crystal of **16**·ethanol (Fig. 12a) form intermolecular hydrogen bonds with a non-coordinated nitrogen atom of adjacent **L8** and with two oxygen atoms of two ethanol molecules, constructing a quasi-2D structure. The NH_3 groups in the crystal of **17**·2(CH_3)₂CO (Fig. 12b) form hydrogen bonds with the oxygen atoms of the solvate molecules. The angles between the pyrimidyl groups and the Cp rings of **L8** in **11–17** vary in the range of 0.6 to 44.5°, which provides their coordination complexes with structural variety.

L9 coordinates to a metal ion only via the 4-nitrogen atom of the pyrazine ring, constructing discrete complexes. In the 1:2 M:L complex $[\text{Cu}(\text{hfac})_2(\text{L9})_2]$ (**18**, Fig. 13a) [67], the geometry around the copper(II) center is a six-coordinate octahedron in which two nitrogen atoms from two **L9** ligands occupy the *trans* positions. A related complex $[\text{Cu}(\text{NO}_3)_2(\text{L9})_2]$ (**19**, Fig. 13b) has a square planar copper(II) center coordinated with two *trans* nitrogen atoms from two **L9** ligands [67]. The angles between the pyrazyl and Cp rings of the ligands in **18** and **19** are 3.7 and 26.3°, respectively.

2.1.3. Naphthyridine derivative (**L10**)

Ferrocenes with 8-naphthyridinyl substituents show unique coordination chemistry with metal ions. **L10** can coordinate to metal ions in a monodentate or bidentate chelate fashion to produce a series of unique complexes with various M:L stoichiometries. Metal complexes with **L10** are discussed in Bera's review [69]; hence we omit discussion on some of their complexes. The

reaction of $\text{PdCl}_2(\text{CH}_3\text{CN})_2$ and **L10** generates the 1:1 M:L complex $[\text{PdCl}_2(\text{L10})]$ (**20**) [70], which catalyzes the methoxycarbonylation of styrene; however, the performance in terms of activity and selectivity is very low compared with related complexes. The reaction of $[\text{Ir}(\text{cod})(\text{L10})_2]\text{BF}_4$ (**21**) and CO in CH_2Cl_2 results in the formation of a dimer complex, $[\text{IrCl}_2(\text{CO})_2(\text{L10})]_2$ (**22**, Fig. 14) [70, 71]. The chlorides are from the solvent molecules. In this complex, the monomer units are linked by an unsupported iridium(II)–iridium(II) bond (2.7121(8) Å).

2.2. *N*-Heterocyclic ferrocenes that produce metallacycle complexes

Structural formulae of *N*-heterocyclic ferrocenes producing metallacycle complexes are summarized in Fig. 15. The chemical formulas of their complexes are listed in Table 2. *N*-heterocycles with a ferrocenyl group attached to the next carbon atom to the nitrogen atom have the ability to produce metallacycle complexes via ortho-metalation (Fig. 16). Some of the complexes show good catalytic activity.

2.2.1. Imidazoline derivatives (**L11**, **L12**)

The reactions of ferrocenyylimidazoline **L11** or **L12** and palladium salts in the presence of a base generate chloride-bridged palladacycle dimers $[\text{Pd}(\mu\text{-Cl})(\text{L})]_2$ {**L** = **L11'** (**23**), **L12'** (**24**)} [72, 73], where the prime indicates that the ligand is deprotonated at the α -carbon atom of the ferrocenyl moiety; hereinafter the same meaning is applied. Although their crystal structures have not been determined, their PPh_3 adducts $[\text{PdCl}(\text{L})\text{PPh}_3]$ {**L** = **L11'** (**25**), **L12'** (**26**, Fig 17)} have been crystallographically characterized [72]. They are stable in air and moisture, which offers advantages to catalytic processes. The coordination geometries around the palladium(II) centers of **25** and **26** are similar to each other, where the phosphine atom is *trans* to the nitrogen atom.

23 has been employed for aza-Claisen rearrangement of *N*-*p*-methoxyphenylbenzimidate to generate *N*-allyl-*N*-(*p*-methoxyphenyl)benzamide [74]. The complex catalyzes the coupling reaction of 4-bromotoluene and phenylboronic acid to give 4-methy-1,1'-biphenyl. The reaction is achieved at low catalyst loading and short reaction time; however, a high temperature is required. **26** activates

the C–Cl bond in aryl chlorides and is employed as the catalyst for the coupling reaction of 4-nitrochlorobenzene and phenylboronic acid in aqueous media to give 4-nitro-1,1'-biphenyl [71]. This catalyst, however, requires a higher temperature and longer reaction time than the water soluble Pd(II)–diimine catalyst [75].

2.2.2. Pyridine and pyrimidine derivatives (**L13**–**L15**)

L13 usually behaves as a monodentate ligand and generates discrete metal complexes; however, their crystal structures have not been reported to the best of our knowledge. In contrast, many metallacycle complexes with **L13'** have been crystallographically studied. The reaction of **L13** with Li_2PdCl_4 generates a 1:2 M:L complex $[\text{PdCl}_2(\text{L13})_2]$ (**27**) [60]. When a similar reaction is carried out in the presence of NaOAc, ortho-metalation occurs at the Cp ring, and a 2:2 M:L chloride-bridged palladacycle dimer $[\text{Pd}(\mu\text{-Cl})(\text{L13}')_2]$ (**28**) is generated [76]. **28** is the precursor of palladacycle complexes $[\text{PdCl}(\text{L13}')\text{PPh}_3]$ and $[\text{Pd}(\text{acac})(\text{L13}')]$ [76]. The reaction of **L13** and a polymeric complex $[\text{RuCl}_2(\text{CO})_2]_n$ in the presence of Na_2CO_3 leads to the formation of a 2:2 M:L chloride-bridged ruthenocycle dimer complex, $[\text{Ru}(\mu\text{-Cl})(\text{L13}')(\text{CO})_2]_2$ (**29**, Fig. 18) [77, 78], which has a planar chirality at the ruthenocycle. The two ruthenocycle units in **29** are perpendicular to each other. This contrasts with other relevant complexes such as *cis*- $[\text{Ru}(\mu\text{-Cl})(\text{ptpy})(\text{CO})_2]_2$, in which the ruthenocycle units show a parallel arrangement [79]. **29** is also a precursor of related complexes, $[\text{PPN}][\text{RuCl}_2(\text{L13}')(\text{CO})_2]$ and $[\text{Ru}(\text{N}^{\wedge}\text{N})(\text{L13}')(\text{CO})_2]$ ($\text{N}^{\wedge}\text{N}$ = chiral bidentate ligands) [77].

A palladacycle complex $[\text{PdCl}(\text{L14}')(\text{iPrNHC})]$ (**30**, Fig. 19) [80], having the advantage of being air-stable, has been tested as a catalyst for both the Suzuki coupling and the Buchwald–Hartwig amination reactions in a PEG media. High activities have been observed when high temperatures and long reaction time are applied. The catalyst can be recycled and reused three times without lessening of activity.

The reactivity and structure of a palladacycle dimer $[\text{Pd}(\mu\text{-Cl})(\text{L15}')_2]$ (**31**) are similar to that found in **28** [81]. In **31**, one of the two nitrogen atoms of the pyrimidine ring remains vacant. The

complex is a precursor for several phosphine complexes, such as $[\text{PdCl}(\mathbf{L15}')(P\text{-donor})]$ ($P\text{-donor} = \text{PPh}_3, \text{PCy}_3, \text{PCy}_2(2\text{-biphenyl}), \text{dcpab}$ (**32**, Fig. 20)) [81]. The coordination environment around the metal center of **32** is similar to that in **26**. Compound **32** shows a catalytic activity for the Buchwald–Hartwig amination, catalyzing the coupling of 2-chloroanisole and 2,5-dimethylaniline.

2.2.3. Bipyridine, quinoline, and phenanthroline derivatives (**L16–L19**)

Many ferrocenyl-bipyridine derivatives and their metal complexes have been prepared; however, their crystal structures are rather limited [82–85].

L16 undergoes an ortho-metalation when reacted with $\text{PdCl}_2(\text{cod})$, and subsequently produces a 1:1 M:L palladacycle complex, $[\text{PdCl}(\mathbf{L16}')](\mathbf{33})$ [86], in which **L16'** behaves as a CNN ligand. Although ortho-metalation generally requires a base to remove the α proton, this reaction proceeds without a base. When treated with *t*-BuNC, **33** produces $[\text{Pd}(\mathbf{L16}')(t\text{-BuNC})]\text{Cl}$ (**34**) [87], showing no successive isocyanide insertion (Fig. 21). The reaction of $\text{PdCl}_2(\text{cod})$ and **L17** affords a 1:1 M:L palladacycle complex, $[\text{PdCl}(\mathbf{L17}')](\mathbf{35})$, Fig. 22) [86]. In **35**, the ferrocenyl rings adopt a synclinal conformation and the two bipyridine rings are approximately parallel to each other. One of the two bipyridyl groups is nearly planar and coordinates to a square planar palladium(II) ion in a CNN fashion, while the other is twisted and without coordination.

L18 acts as a bidentate ligand in the 1:1 M:L complex $[\text{ZnCl}_2(\mathbf{L18})](\mathbf{36})$, Fig. 23) [88], which exhibits a metallacycle structure. The ligand coordinates to the zinc(II) ion via the nitrogen atom of the quinoline ring and a carbon atom of the Cp ring, where the Zn–C distance is 2.407(2) Å. The metal center adopts a distorted tetrahedral coordination geometry. The spacing between adjacent naphthalene rings is 3.39 Å, which falls within a $\pi \cdots \pi$ interaction distance.

The reaction of $\text{Pd}(\text{OAc})_2$ and **L19** in the presence of $\text{CF}_3\text{CO}_2\text{H}$ affords a palladacycle complex, $[\text{Pd}(\text{O}_2\text{CCF}_3)(\mathbf{L19}')](\mathbf{37})$, Fig. 24) [89]. This complex is used for the preparation of $[\text{Pd}(\mathbf{L19}')(\text{MeCN})]\text{PF}_6$, $[\text{Pd}(\mathbf{L19}')(\text{PPh}_3)](\text{O}_2\text{CCF}_3)_2$, and $[\{\text{Pd}(\mathbf{L19}')\}_2(\mu\text{-P}^*\text{P})](\text{O}_2\text{CCF}_3)_2$ ($\text{P}^*\text{P} = \text{dppe}, \text{dppp}$), owing to the lability of the CF_3CO_2 anion. The reaction of K_2PdCl_4 and **L19** generates the palladacycle complex $[\text{PdCl}(\mathbf{L19}')](\mathbf{38})$ [90]. The coordination geometries around the metal

centers in **37** and **38** are similar to each other.

2.3. *N*-Heterocyclic ferrocenes that produce chelate complexes

Structural formulae of *N*-heterocyclic ferrocenes producing chelate complexes are summarized in Fig. 25. The chemical formulas of their complexes are listed in Table 3. These complexes have been studied mainly in terms of structural chemistry; however, several metal complexes with polypyridinyl ferrocenes have been employed for DNA binding and DNA photocleavage reagents.

2.3.1. Pyrazole and triazole derivatives (**L20**–**L23**)

The heptanuclear wheel-like complex $[\text{Ni}_7(\text{OH})_4(\text{L20})_8](\text{ClO}_4)_2 \cdot 6\text{CH}_3\text{CN}$ (**39**, Fig. 26) is obtained by the reaction of **L20** and $\text{Ni}(\text{ClO}_4)_4 \cdot 6\text{H}_2\text{O}$ in the presence of a base [91]. This complex is composed of nickel(II) ions with four different types of coordination geometries, including a NiN_2O_4 octahedron, a NiN_5O octahedron, two NiN_3O_2 square pyramids, and two NiN_3O square planes. The NiN_2O_4 octahedron is located at the center of the wheel, while the other nickel(II) ions are linked by six **L20** ligands to construct a macrocycle. The temperature dependence of the magnetic susceptibility shows the presence of antiferromagnetic interactions ($\theta = -22.5$ K) between the nickel(II) ions.

An *N*-alkylated ligand **L21** has been obtained by the treatment of **L20** with NaH and $\text{BrCH}_2\text{COOC}_2\text{H}_5$. The reaction of **L21** and $\text{Mo}(\text{CO})_4(\text{piperidine})_2$ affords the 1:1 M:L complex $[\text{Mo}(\text{CO})_4(\text{L21})]$ (**40**, Fig. 27), in which the ligand coordinates to the molybdenum(0) center in an NN bidentate chelate fashion [92].

A tridentate ligand **L22** can be prepared from **L2**. The reaction of **L22** and $\text{Fe}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ in acetonitrile affords a pentanuclear complex, $[\text{Fe}(\text{L22})_2](\text{BF}_4)_2 \cdot 3\text{CH}_3\text{CN}$ (**41**, Fig. 28) [93]. The coordination geometry around the iron(II) center is a highly distorted octahedron, in which **L22** occupies the meridional positions of the iron(II) ion. The Fe–N lengths of the complex are relatively long, being characteristic for a high spin state of iron(II) ion. The complex does not show a spin

conversion even at low temperature, owing to the distorted geometry that stabilizes the high spin state.

A nitrogen-rich ligand **L23** acts as a chemical sensor for toxic heavy metal ions [94]. Addition of cadmium(II), lead(II), and mercury(II) to an acetonitrile solution of **L23** increases the half-wave redox potential ($E_{1/2}$) of the ferrocenyl moiety. The reaction of **L23** with $\text{Zn}(\text{OTf})_2$ yields the 1:2 M:L complex $[\text{Zn}(\text{OTf})_2(\text{L23})_2] \cdot \text{CHCl}_3$ (**42**, Fig. 29) [94], in which the distorted octahedral zinc(II) ion is coordinated with four equatorial nitrogen atoms from two **L23** and axial oxygen atoms of OTf^- anions.

2.3.2. Bipyridine and pyrimidine derivatives (**L16**, **L24**)

As described above, **L16** can act as NN-bidentate chelate and CNN-tridentate ligands. The 1:2 M:L complex $[\text{Co}(\text{L16})_2(\text{CH}_3\text{CN})_2](\text{OTf})_2$ (**43**, Fig. 30) possesses an octahedral cobalt(II) center coordinated by two **L16** ligands in a chelate fashion and two acetonitrile molecules occupying the *cis* positions [95].

The complexes $[\text{Cu}(2,9\text{-dianthryl-1,10-phenanthroline})(\text{L24})]\text{BF}_4$ ($R = p\text{-tolyl}$, 1-naphthyl, 9-anthracenyl, and *t*-butyl) (**44**) contain a tetrahedral copper(I) center coordinated with two bulky ligands in a chelate fashion [96, 97]. In the solution state, the ferrocene group in **44** is located near the copper(I) center in the neutral state (Fig. 31a), whereas it is placed far away from the copper(I) center in the oxidized state owing to the electrostatic repulsion between the copper(I) center and the ferricinium moiety (Fig. 31b). Therefore, these complexes exhibit redox-driven conformational switching, which may further lead to interesting molecular functions.

2.3.3. Terpyridine and polypyridine derivatives (**L25**, **L26**)

Similar to the ferrocenyl-bipyridine derivatives, several positional isomers of ferrocenyl-terpyridine derivatives have been prepared [84, 98]; however, only **L25** has been extensively studied as a ligand [99–101]. The 1:1 M:L complex $[\text{Cu}(\text{dppz})(\text{L25})](\text{ClO}_4)_2$ (**45**) shows DNA binding and photoinduced DNA cleavage activities [102]. The analogues $[\text{M}(\text{N}^{\wedge}\text{N})(\text{L25})]\text{X}_2$

{ $M = \text{Cu}$, $N^{\wedge}N = \text{dppz}$, $X = \text{ClO}_4^-$ (**46**, Fig. 32) [102]; $M = \text{Cu}$, $N^{\wedge}N = \text{bpy}$, $X = \text{BF}_4^-$ (**47**) [103]; $M = \text{Cu}$, $N^{\wedge}N = \text{phen}$, $X = \text{ClO}_4^-$ (**48**) [104]; $M = \text{Zn}$, $N^{\wedge}N = \text{phen}$, $X = \text{ClO}_4^-$ (**49**) [105]; $M = \text{VO}$, $N^{\wedge}N = \text{bpy}$, $X = \text{PF}_6^-$ (**50**) [106]} have been crystallographically characterized. **46** has a distorted square pyramidal copper(II) center. In **46**, **L25** and one of the two pyrido nitrogen atoms of dppz occupy the equatorial plane of the metal center, while the remaining pyrido nitrogen atom is located at the axial position. The coordination geometries around the metal centers of **47–50** resemble that of **46**. In **50**, the coordination geometry of vanadium(IV) is approximately octahedral, in which the three nitrogen atoms from **L25** occupy the meridional positions. **L25** can also coordinate to three different metal ions using its three pyridyl nitrogen atoms. The reaction of three equivalents of $\text{Au}(\text{C}_6\text{F}_5)(\text{THF})$ and **L25** affords a 3:1 M:L complex, $[\{\text{Au}(\text{C}_6\text{F}_5)\}_3(\text{L25})]$ (**51**, Fig. 33) [107], in which the three pyridyl nitrogen atoms coordinate to three different gold(I) ions. The three gold(I) ions are linked by **L25** and aurophilic interactions of themselves, in which the central gold(I) ion adopts a distorted square planar coordination and the outer two gold(I) ions adopt a T-shaped coordination geometry. The outer two pyridyl nitrogen atoms point in almost opposite directions.

The polypyridine ligand **L26** may behave as either a multidentate or a bridging ligand to produce complexes with 1:1, 2:2, and 2:1 M:L ratios. The 2:2 M:L complex $[\text{Ag}(\text{L26})_2(\text{OTf})_2]$ (**52**, Fig. 34) has a double-helical structure in which the two silver(I) ions have different coordination environments [108]. One is an elongated trigonal bipyramid, and the other has a geometry intermediate between tetrahedron and square plane. The distance between the silver(I) ions is 3.089(2) Å, which is an acceptable distance for argentophilic interactions [109–111]. A similar double-helical structural motif is found in $[\text{M}(\text{solv})(\text{L26})_2(\text{PF}_6)_n]$ [112] [$M = \text{Cu}$, solv = none, $n = 3$ (**53**, Fig. 35a); $M = \text{Ni}$, solv = H_2O , $n = 4$ (**54**)], in which one of the two metal centers adopts a six-coordinate geometry and the other shows a four coordinate geometry. The six- and four-coordinate metal centers in **53** are copper(II) and copper(I) ions, respectively; thus the complex is in a mixed valence state. The metal centers in 1:1 M:L complexes $[\text{M}(\text{H}_2\text{O})_2(\text{L26})](\text{PF}_6)_2$ [$M = \text{Fe}$ (**55**), Co (**56**)] (Fig. 35b) adopt a hepta-coordinate geometry [113], which is occupied by five nitrogen atoms from **L26** and two oxygen atoms from two water molecules. A helical complex

$[\text{Ru}_2\text{Cl}(\text{L25})_2(\text{L26})](\text{PF}_6)_3$ (**57**, Fig. 35c) includes two different six-coordinate ruthenium(II) centers [112]. One of the two ruthenium centers is coordinated by three nitrogen atoms from **L25** and three nitrogen atoms from **L26**, while the other is surrounded by two nitrogen atoms from **L25**, three nitrogen atoms from **L26** and a chloride anion.

2.3.4. Hydroxyquinoline and phenanthroline derivatives (**L27**, **L19**)

The reaction of hydroxyquinoline derivative **L27** and metal salts produces $[\text{M}(\text{L27})_2(\text{H}_2\text{O})_2]$ [$\text{M} = \text{Ni}$ (**58**), Cu (**59**)] [113]. They adopt a six-coordinate octahedral geometry, in which two nitrogen atoms and two phenoxy oxygen atoms are from the ligands and two oxygen atoms are from two coordinated water molecules.

The reaction of phenanthroline derivative **L19** and a palladium(II) salt produces a complex with chelate bidentate or CNN tridentate coordination modes depending on experimental conditions. A chelate complex $[\text{PdCl}_2(\text{L19})]$ is obtained by the reaction of **L19** and $\text{PdCl}_2(\text{cod})$ [86], while the palladacycle complex $[\text{PdCl}(\text{L19}')](\text{38})$ is generated by the reaction of **L19** and K_2PdCl_4 [90]. The treatment of $[\text{PdCl}(\text{CH}_3)(\text{L19})]$ (**60**) with AgPF_6 in CH_3CN leads to the formation of $[\text{Pd}(\text{CH}_3)(\text{CH}_3\text{CN})(\text{L19})]$ (**61**) [89], which shows excellent catalytic activity in the Heck reaction of iodobenzene and methylacrylate to afford methyl-*trans*-cinnamate.

2.4. *N*-Heterocyclic ferrocenes that produce macrocyclic complexes

Structural formulae of *N*-heterocyclic ferrocenes producing macrocyclic complexes are summarized in Fig. 36. The chemical formulae of their complexes are listed in Table 4. 1,1'-Bis substituted ferrocenes with *N*-heterocycles of six-membered rings and condensed aromatic rings are likely to adopt the *syn* conformation and therefore afford discrete metal complexes, although they are capable of adopting other conformations. This is associated with the intramolecular $\pi \cdots \pi$ interaction between the *N*-heterocyclic rings.

In 1,1'-bis substituted ferrocenes, the torsion angle τ is used to express the conformation, which is defined as the torsion angle of $\text{X}^1\text{--Cp}^1\text{--Cp}^2\text{--X}^2$, where X^1 and X^2 are carbon atoms bonded

to *N*-heterocycles, and Cp^1 and Cp^2 are the centroids of the Cp rings (Fig. 37) [11]. The variety of torsion angles of the ferrocene backbone provides *N*-heterocyclic ferrocene complexes with structural versatility.

2.4.1 Pyrazole derivative (**L1**)

The reaction of **L1**·H and $[\text{Rh}(\mu\text{-Cl})(\text{cod})]_2$ in the presence of a base generates the macrocyclic complex $[\text{Rh}(\mu\text{-L1})(\text{cod})]_2$ (**62**, Fig. 38) [114]. The complex adopts a head-to-tail structure in which the -Rh-N-N-Rh-N-N- metallacycle exhibits a boat conformation.

2.4.2. Pyridine and pyrazine derivatives (**L28–L31**)

Ditopic ligands **L28** and **L29** show either chelating or bridging coordination modes to construct 2:2, 1:1, and 2:1 M:L complexes. The 2:2 M:L dimeric complex $[\text{Ag}(\mu\text{-ClO}_4)(\text{L28})]_2$ (**63**, Fig. 39a) contains two $\text{Ag}(\text{L28})$ units which are linked by two ClO_4^- counter anions [115]. The **L28** ligand in **63** adopts a synclinal conformation ($\tau = 84.2^\circ$) and coordinates to silver(I) ion with the *trans* chelating mode ($\text{N-Ag-N} = 163.1^\circ$). The **L28** ligand in 1:1 M:L $[\text{Pd}(\text{CH}_3)\text{Cl}(\text{L28})]$ (**64**, Fig. 39b) adopts a synclinal conformation ($\tau = 0.4^\circ$) and chelates to palladium(II) ion in the *cis* mode ($\text{N-Pd-N} = 84.5^\circ$) [116]. The complex shows C=O insertion into the Pd-CH_3 bond to generate $[\text{Pd}(\text{COCH}_3)\text{Cl}(\text{L28})]$ (**65**) [116]. The coordination chemistries of octamethylated **L29** are similar to those of **L28**. The ligand conformations in 2:1 M:L $[\text{Cu}(\text{L29})][\text{CuCl}_2]$ (**66**, Fig. 39c) and 1:1 M:L $[\text{Cu}(\text{L29})]\text{BF}_4$ (**67**) are similar to that in **61** [117,118]. In contrast to **63** and **64**, in the 2:1 M:L complex $[\{\text{PtCl}_2(\text{C}_2\text{H}_4)\}_2(\mu\text{-L28})]$ (**68**, Fig. 39d) [116], **L28** bridges metal ions. The two pyridine rings of **L28** in the complex lie approximately parallel and are separated by 3.65 Å, which is an acceptable distance for $\pi\cdots\pi$ interactions. The molecular structure of 2:1 M:L $[\{\text{PtCl}_2(\text{C}_2\text{H}_4)\}_2(\mu\text{-L29})]$ (**69**) is almost identical to that of **68** [118].

L30 cannot chelate to a metal ion and has a tendency to adopt the *syn* conformation, causing its complex to form 2:2 M:L metallomacrocyclic structures. Indeed, coordination polymer complexes containing **L30** with an *anti* conformation have not been reported. In the

metallomacrocyclic $[\text{AgNO}_3(\text{L30})]_2 \cdot 1.5\text{H}_2\text{O}$ (**70**, Fig. 40a) [119, 120], the two pyridine rings of **L30** are in a face-to-face orientation, with the distance between the two pyridine rings being 3.44 Å. The silver(I) ions are coordinated in a highly distorted tetrahedral geometry by two nitrogen atoms from two **L30** ligands and two oxygen atoms from the NO_3^- anion. One of the two anions links adjacent macrocyclic units. The macrocyclic complex $[\text{Zn}(\text{OAc})_2(\text{L30})]_2$ (**71**, Fig. 40b) contains two zinc(II) ions with a distorted square pyramidal geometry and two **L30** ligands with a synperiplanar conformation ($\tau = 3.6^\circ$) [119]. Two of the four OAc^- anions bridge the two zinc(II) ions in the macrocycle with a monoatomic μ^2 -bridging mode, while the others coordinate to the ions with a monodentate *syn* fashion. The crystal structure of $[\text{Cd}(\text{OAc})_2(\text{L30})]_2 \cdot \text{CH}_3\text{OH} \cdot 0.5\text{C}_6\text{H}_6$ (**72**) is somewhat similar to that of **71** [119]. The butterfly shaped complex $[\text{ZnCl}_2(\text{L30})]_2$ (**73**, Fig. 40c) is composed of two zinc(II) ions with a tetrahedral geometry and two **L30** ligands with a synclinal conformation ($\tau = 35.1^\circ$) [119, 120]. In **70–72**, the pyridine rings in **L30** are approximately parallel and are twisted with respect to the attached Cp rings by 3.5–14.8°. Comparison of the zinc(II) complexes **71** and **73** reveals the correlation between the $\text{Zn} \cdots \text{Zn}$ and $\text{Fe} \cdots \text{Fe}$ distances and the conformation of **L30**. The $\text{Zn} \cdots \text{Zn}$ and $\text{Fe} \cdots \text{Fe}$ distances of **71** with a synperiplanar **L30** are 3.9 and 15.0 Å, respectively, whereas those of **73** with a synclinal **L30** are 6.1 and 11.9 Å, respectively.

The 1,1'-di-substituted ligand **L31** tends to adopt the synperiplanar conformation, probably owing to an intramolecular $\pi \cdots \pi$ interaction between the two pyrazine rings. The pyrazine rings in **L31** may lie in the same direction or different directions; hence the ligand can afford macrocyclic or polymer complexes when reacted with metal salts. The copper(I) complex $[(\text{CuI})_2(\text{L31})]_2 \cdot \text{L31}$ (**74**, Fig. 41a) contains a ladder-like $(\text{CuI})_4(\text{L31})_2$ unit and a free **L31** [121]. The ladder-like unit consists of three $(\text{CuI})_2$ cyclic units and two **L31** ligands with a synperiplanar conformation. In the crystal, the free **L31** adopts an antiperiplanar conformation and occupies the space between the ladder-like units. The reaction of AgX and **L31** affords a series of metallomacrocycles $[\text{AgX}(\text{L31})]_2 \cdot (\text{solv})$ [$\text{X} = \text{ClO}_4^-$, $\text{solv} = 2\text{C}_6\text{H}_6$ (**75**, Fig. 41b); $\text{X} = \text{ClO}_4^-$, $\text{solv} = \text{none}$; $\text{X} = \text{NO}_3^-$, $\text{solv} = \text{C}_6\text{H}_6$; $\text{X} = \text{NO}_3^-$, $\text{solv} = \text{PhCl}$; $\text{X} = \text{NO}_3^-$, $\text{solv} = \text{PhCH}_3$; $\text{X} = \text{PF}_6^-$, $\text{solv} = \text{none}$] with various $\text{Ag} \cdots \text{Ag}$ distances [121]. The macrocyclic unit in **75** is composed of two silver(I) ions with a highly distorted tetrahedral

geometry, which are bridged by the two **L31** ligands and two counter anions, constructing a paddle-windmill-like structure. The other macrocyclic complexes exhibit almost identical structures. The Ag \cdots Ag distances in these units can be changed by changing the counter anions (PF $_6^-$ = ca. 3.4 Å; ClO $_4^-$ = ca. 3.4–3.3 Å; NO $_3^-$ = ca. 3.2 Å). The difference in the Ag \cdots Ag distances between the ClO $_4^-$ and NO $_3^-$ complexes is ascribable to the differences in the negative charge density on the oxygen atoms of the counter anions.

2.4.3. Quinoline and naphthyridine derivatives (**L32**, **L33**)

The 1,1-disubstituted ligand **L32** acts as a tridentate ligand in [ZnCl(**L32**)] $_2$ [Zn $_2$ Cl $_6$] (**76**, Fig. 42) [122], with the ligand coordinating to a zinc(II) ion by the two nitrogen atoms of the quinoline rings and the iron(II) atom in the ferrocenyl group. The complex consists of two 1:1 M:L cation [ZnCl(**L32**)] $^+$ units and a dianion [Zn $_2$ Cl $_6$] $^{2-}$ unit. The zinc(II) center in the cation adopts a distorted tetrahedral geometry and is coordinated by **L32** in a tridentate fashion and by a chlorine atom. The zinc(II)–iron(II) distance is 2.562(1) Å. The ferrocenyl moiety adopts a synclinal conformation.

The tetramer complex [ZnCl $_2$ (**L33**)] $_4$ (**77**, Fig. 43) possesses a macrocyclic structure [123, 124], in which **L33** behaves as a bridging ligand and adopts a synclinal conformation ($\tau = 2.5^\circ$). In **77**, the two naphthyridine rings of **L33** form $\pi\cdots\pi$ interactions (3.37 Å) and coordinate to two different zinc(II) ions with the nitrogen atoms far from ferrocene group. The reaction of Cu(CH $_3$ CN) $_4$ ·ClO $_4$ and **L33** affords complexes with various M:L stoichiometries [Cu(**L33**)] $_2$ (ClO $_4$) $_2$ (**78**), [Cu(**L33**)]ClO $_4$ (**79**), and [Cu $_2$ (ClO $_4$)(**L33**)]ClO $_4$ (**80**) [123, 124], depending on the initial ratio of M:L. The crystal structure of **78**·4CH $_3$ NO $_2$ reveals that it adopts a 2:2 M:L macrocyclic structure (Fig. 44a), in which the copper(I) ions show a linear coordination geometry occupied by two nitrogen atoms farthest from the ferrocene groups of two **L33** ligands. The intramolecular Cu \cdots Cu distance is 3.27 Å, suggesting no significant interaction between them. In the complex, the ferrocenyl moiety adopts a synclinal conformation ($\tau = 3.7^\circ$) and the two naphthyridine rings of **L33** stack in a head-to-head orientation (3.53 Å). **80** shows a 2:1 M:L macrocyclic structure (Fig. 44b), in which one of the copper(I) ions, coordinated by the nitrogen atoms near the ferrocenyl group of

L33, adopts a nearly linear geometry. The other copper(I) ion has a T-shaped coordination geometry, surrounded by two nitrogen atoms farther from the ferrocenyl group in **L33** and a oxygen atom from the ClO_4^- anion. There is no significant interaction between the copper(I) ions (2.47 Å). **L33** adopts a synclinal conformation ($\tau = 80.2^\circ$) in the complex.

3. Summary and future outlook

The structural aspects of *N*-heterocyclic ferrocene complexes have been discussed in detail in this review. Many *N*-heterocyclic ferrocenes have been known for years; however, it is only rather recently that they have been exploited as ligands and chemical sensors. These *N*-heterocyclic ferrocenes show interesting coordination chemistry, in which they act as monodentate, bidentate, multidentate, or bridging ligands depending mainly on the ligand design, namely the size, shape, and number of nitrogen atoms of the *N*-heterocycles. In addition, we have briefly discussed applications of these complexes for catalysts and redox-driven conformational switching.

In the future, the design and use of ferrocene derivatives bearing nitrogen-rich *N*-heterocycles will in future become a more active area because of their potential to produce metallacycle and hetero-polynuclear complexes with unique properties. As described above, such complexes have played roles in many important areas from catalysis chemistry to material chemistry. In addition, the development of redox-switchable materials, such as electrochromic dyes, or catalysts which can be tuned “on/off” by an external potential, is also an interesting research target.

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Table 1

Metal complexes with monodentate *N*-heterocyclic ferrocenes.

Number	Complex	Figure	Reference
1	[W(CO) ₅ (L1 ·H)]	5	[49]
2	[Zn(NO ₃) ₂ (L2 ·H) ₄]	6a	[50]
3	[CoCl ₂ (L2 ·H) ₄]	6b	
4	[Zn(NCS) ₂ (L2 ·H) ₂]	6c	
5	[PdCl ₂ (L3) ₂]	7	[51]
6	[PdCl ₂ (L4) ₂]	-	[52]
7	[PdCl ₂ (L5) ₂]	9a	[59]
8	[PtCl ₂ (L5) ₂]	9b	[60]
9	[Au(C ₆ F ₅)(L5) ₂]	9c	[61]
10	[PdCl ₂ (L7) ₂]	10	[64]
11	[Cu(OAc) ₂ (L8) ₂]	11a	[65]
12	[Zn(NCS) ₂ (L8) ₂]	11b	
13	[Ni(hfac) ₂ (L8) ₂]	11c	[67]
14	[Zn(NO ₃) ₂ (L8) ₃]	11d	[65]
15	[Ni(NCS) ₂ (L8) ₄]	11e	[67]
16	[<i>cis</i> -Pt(NH ₃) ₂ (L8) ₂](PF ₆) ₂	12a	[68]
17	[<i>trans</i> -Pt(NH ₃) ₂ (L8) ₂](PF ₆) ₂	12b	
18	[Cu(hfac) ₂ (L9) ₂]	13a	[67]
19	[Cu(NO ₃) ₂ (L9) ₂]	13b	
20	[PdCl ₂ (L10)]	-	[70]
21	[Ir(cod)(L10) ₂]BF ₄	-	[70,71]
22	[IrCl ₂ (CO) ₂ (L10) ₂]	14	

Table 2

Metallacycle complexes from *N*-heterocyclic ferrocenes.

Number	Complex	Figure	Reference
23	[Pd(μ-Cl)(L11')] ₂	-	[72,73]
24	[Pd(μ-Cl)(L12')] ₂	-	
25	[PdCl(L11')PPh ₃]	-	[72]
26	[PdCl(L12')PPh ₃]	17	
27	[PdCl ₂ (L13) ₂]	-	[60]
28	[Pd(μ-Cl)(L13')]	-	[76]
29	[Ru(μ-Cl)(L13')(CO) ₂] ₂	18	[77,78]
30	[PdCl(L14')(<i>i</i> PrNHC)]	19	[80]
31	[Pd(μ-Cl)(L15')]	-	[81]
32	[PdCl(L15')(dcpab)]	20	
33	[PdCl(L16')]	21	[86]
34	[Pd(L16')(<i>t</i> -BuNC)]Cl		[87]
35	[PdCl(L17')]	22	[86]
36	[ZnCl ₂ (L18)]	23	[88]
37	[Pd(O ₂ CCF ₃)(L19')]	24	[89]
38	[PdCl(L19')]	-	[90]

Table 3

Chelate complexes with *N*-heterocyclic ferrocenes.

Number	Complex	Figure	Reference
39	[Ni ₇ (OH) ₄ (L20) ₈](ClO ₄) ₂ ·6CH ₃ CN	26	[91]
40	[Mo(CO) ₄ (L22)]	27	[92]
41	[Fe(L22) ₂](BF ₄) ₂ ·3CH ₃ CN	28	[93]
42	[Zn(OTf) ₂ (L23) ₂]·CHCl ₃	29	[94]
43	[Co(L16) ₂ (CH ₃ CN) ₂](OTf) ₂	30	[95]
44	[Cu(2,9-dianthryl-1,10-phenanthroline)(L24)]BF ₄	31	[96,97]
45	[Cu(dppz)(L25)](PF ₆) ₂	-	[102]
46	[Cu(dppz)(L25)](ClO ₄) ₂	32	
47	[Cu(bpy)(L25)](BF ₄) ₂	-	[103]
48	[Cu(phen)(L25)](ClO ₄) ₂	-	[104]
49	[Zn(phen)(L25)](ClO ₄) ₂	-	[105]
50	[VO(bpy)(L25)](PF ₆) ₂	-	[106]
51	[{Au(C ₆ F ₅) ₃ (L25)}	33	[107]
52	[Ag(L26) ₂](OTf) ₂	34	[108]
53	[Cu(L26) ₂](PF ₆) ₃	35a	[112]
54	[Ni(H ₂ O)(L26) ₂](PF ₆) ₄	-	
55	[Fe(H ₂ O) ₂ (L26)](PF ₆) ₂	35b	[113]
56	[Co(H ₂ O) ₂ (L26)](PF ₆) ₂		
57	[Ru ₂ Cl(L25) ₂ (L26)](PF ₆) ₃	35c	[112]
58	[Ni(L27) ₂ (H ₂ O) ₂]	-	[113]
59	[Cu(L27) ₂ (H ₂ O) ₂]	-	
60	[PdClCH ₃ (L19)]	-	[89]
61	[Pd(CH ₃)(CH ₃ CN)(L19)]	-	

Table 4

Macrocyclic complexes with *N*-heterocyclic ferrocenes.

Number	Complex	Figure	Reference
62	[Rh(μ - L1)(cod)] ₂	38	[114]
63	[Ag(μ -ClO ₄)(L28)] ₂	39a	[115]
64	[Pd(CH ₃)Cl(L28)]	39b	[116]
65	[Pd(COCH ₃)Cl(L28)]	-	
66	[Cu(L29)] [CuCl ₂]	39c	[117,118]
67	[Cu(L29)]BF ₄	-	
68	[{PtCl ₂ (C ₂ H ₄)} ₂ (μ - L28)]	39d	[116]
69	[{PtCl ₂ (C ₂ H ₄)} ₂ (μ - L29)]		[118]
70	[AgNO ₃ (L30)] ₂ ·1.5H ₂ O	40a	[119,120]
71	[Zn(OAc) ₂ (L30)] ₂	40b	[119]
72	[Cd(OAc) ₂ (L30)] ₂ ·CH ₃ OH·0.5C ₆ H ₆	-	
73	[ZnCl ₂ (L30)] ₂	40c	[119,120]
74	[(CuI) ₂ (L31)] ₂ · L31	41a	[121]
75	[AgX(L31)] ₂ ·2C ₆ H ₆	41b	
76	[ZnCl(L32)] ₂ [Zn ₂ Cl ₆]	42	[122]
77	[ZnCl ₂ (L33)] ₄	43	[123,124]
78	[Cu(L33)] ₂ (ClO ₄) ₂	44a	
79	[Cu(L33)]ClO ₄	-	
80	[Cu ₂ (ClO ₄)(L33)]ClO ₄	44b	

Figure Captions

Fig. 1. Representative *N*-heterocycles that are used as substituents to ferrocenes.

Fig. 2. Conformational flexibility of ferrocene rings and *N*-heterocycles (e.g. 1,1'-bis(2-pyridyl)ferrocene).

Fig. 3. Possible coordination modes of *N*-heterocyclic ferrocenes.

Fig. 4. *N*-Heterocyclic ferrocenes that adopt monodentate coordination.

Fig. 5. 1D hydrogen bonding network structure of **1**. Dotted lines indicate hydrogen bonds. Hydrogen atoms bonded to carbon atoms are omitted for clarity, similarly hereinafter.

Fig. 6. (a) 1D hydrogen bonding network structure of **2a**, (b) molecular structure of **3**, and (c) 1D hydrogen bonding network structure of **4**. Dotted lines indicate hydrogen bonds.

Fig. 7. Molecular structure of **5**.

Fig. 8. Schematic illustration of the complexation of ferrocenyltriazole and β -cyclodextrin.

Fig. 9. Molecular structures of (a) **7**, (b) **8**, and (c) **9**. Dotted line indicates Au \cdots Au aurophilic interactions.

Fig. 10. Schematic drawing of the molecular structure of **10**.

Fig. 11. Molecular structures of (a) **11**, (b) **12**, (c) **13**, (d) **14**, and (e) **15**.

Fig. 12. Molecular structures of (a) **16**·ethanol and (b) **17**·2(CH₃)₂CO. Solvate molecules are also shown. Dotted lines indicate hydrogen bonds.

Fig. 13. Molecular structures of (a) **18** and (b) **19**.

Fig. 14. Molecular structure of **22**.

Fig. 15. *N*-Heterocyclic ferrocenes that produce metallacycle complexes.

Fig. 16. Ortho-metalation of *N*-heterocyclic ferrocenes.

Fig. 17. Molecular structure of **26**.

Fig. 18. Molecular structure of **29**.

Fig. 19. Molecular structure of **30**.

Fig. 20. Molecular structure of **32**.

Fig. 21. Formation of **34** from **33** and *t*-BuNC.

Fig. 22. Molecular structure of **35**.

Fig. 23. Molecular structure of **36**.

Fig. 24. Molecular structure of **37**.

Fig. 25. *N*-Heterocyclic ferrocenes that produce chelate complexes.

Fig. 26. Molecular structure of **39**. Coordination geometries around the nickel ions are highlighted.

Fig. 27. Molecular structure of **40**.

Fig. 28. Molecular structure of **41**. Counter anions and solvent molecules are omitted for clarity.

Fig. 29. Molecular structure of **42**. Solvent molecules are omitted for clarity.

Fig. 30. Molecular structure of **43**. Counter anions are omitted for clarity.

Fig. 31. Redox-driven conformational change of **44**: (a) neutral and (b) oxidized states.

Fig. 32. Molecular structure of **46**. Counter anions are omitted for clarity.

Fig. 33. Molecular structure of **51**.

Fig. 34. Schematic drawing of the molecular structure of **52**. Dashed line indicates Ag \cdots Ag argentophilic interactions.

Fig. 35. Schematic drawing of the molecular structures of (a) **53**, (b) **55** and **56**, and (c) **57**.

Fig. 36. *N*-Heterocyclic ferrocenes that produce macrocyclic complexes.

Fig. 37. Schematic illustrations of the torsion angle τ and conformational flexibility of 1,1'-disubstituted ferrocenes.

Fig. 38. Molecular structure of **62**.

Fig. 39. Molecular structures of (a) **63** and (b) **64**, (c) **66**, and (d) **68**. Dotted line indicates weak Ag \cdots O interactions.

Fig. 40. Molecular structures of (a) **70**, (b) **71**, and (c) **73**. Solvent molecules are omitted for clarity. Dotted lines indicate weak Ag \cdots O interactions.

Fig. 41. Molecular structures of (a) **74** and (b) **75**. Solvent molecules are omitted for clarity. Dotted lines indicate weak Ag \cdots O interactions.

Fig. 42. Molecular structure of **76**. Counter anions are omitted for clarity.

Fig. 43. Molecular structure of **77**.

Fig. 44. Molecular structures of (a) **78**·4CH₃NO₂ and (b) **80**. Solvent molecules and non-coordinated counter anions are omitted for clarity.